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(54) **Polymerisation process**

(57)   The present invention provides a continuous gas fluidised bed process for the polymerisation of olefin monomer selected from (a) ethylene, (b) propylene (c) mixtures of ethylene and propylene, and (d) one or more other alpha-olefins mixed with (a), (b) or (c), to produce a polymer in a fluidised bed reactor which process comprises:

(1)   continuously recycling a gaseous stream comprising at least some of the olefin monomer through a fluidised bed in said reactor in the presence of a polymerisation catalyst under reactive conditions;

(2)   cooling at least part of said gaseous stream withdrawn from said reactor to a temperature at which liquid condenses out and separating at least part of the condensed liquid from the gaseous stream; and

(3)   introducing at least part of the separated liquid directly into the fluidised bed,

characterised in that the condensed liquid is separated from the gaseous stream in a separator which is integral with the fluidised bed reactor.

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Description

The present invention relates to a continuous process for the gas-phase polymerisation of olefins in a fluidised bed reactor.

Processes for the homopolymerisation and copolymerisation of olefins in the gas phase are well known in the art. Such processes can be conducted for example by introducing the gaseous monomer into a stirred and/or fluidised bed comprising polyolefin and a catalyst for the polymerisation.

In the fluidised bed polymerisation of olefins, the polymerisation is conducted in a fluidised bed reactor wherein a bed of polymer particles is maintained in a fluidised state by means of an ascending gas stream comprising the gaseous reaction monomer. The startup of such a polymerisation generally employs a bed of polymer particles similar to the polymer which it is desired to manufacture. During the course of polymerisation, fresh polymer is generated by the catalytic polymerisation of the monomer, and polymer product is withdrawn to maintain the bed at more or less constant volume. An industrially favoured process employs a fluidisation grid to distribute the fluidising gas to the bed, and to act as a support for the bed when the supply of gas is cut off. The polymer produced is generally withdrawn from the reactor via a discharge conduit arranged in the lower portion of the reactor, near the fluidisation grid. The fluidised bed comprises a bed of growing polymer particles. This bed is maintained in a fluidised condition by the continuous upward flow from the base of the reactor of a fluidising gas.

The polymerisation of olefins is an exothermic reaction and it is therefore necessary to provide means to cool the bed to remove the heat of polymerisation. In the absence of such cooling the bed would increase in temperature and, for example, the catalyst becomes inactive or the bed commences to fuse. In the fluidised bed polymerisation of olefins, the preferred method for removing the heat of polymerisation is by supplying to the polymerisation reactor a gas, the fluidising gas, which is at a temperature lower than the desired polymerisation temperature, passing the gas through the fluidised bed to conduct away the heat of polymerisation, removing the gas from the reactor and cooling it by passage through an external heat exchanger, and recycling it to the bed. The temperature of the recycle gas can be adjusted in the heat exchanger to maintain the fluidised bed at the desired polymerisation temperature. In this method of polymerising alpha olefins, the recycle gas generally comprises the monomeric olefin, optionally together with, for example, an inert diluent gas such as nitrogen or a gaseous chain transfer agent such as hydrogen. Thus, the recycle gas serves to supply the monomer to the bed, to fluidise the bed, and to maintain the bed at the desired temperature. Monomers consumed by the polymerisation reaction are normally replaced by adding make up gas to the recycle gas stream.

It is well known that the production rate (i.e. the space time yield in terms of weight of polymer produced per unit volume of reactor space per unit time) in commercial gas fluidised bed reactors of the afore-mentioned type is restricted by the maximum rate at which heat can be removed from the reactor. The rate of heat removal can be increased for example, by increasing the velocity of the recycle gas and/or reducing the temperature of the recycle gas and/or changing the heat capacity of the recycle gas. However, there is a limit to the velocity of the recycle gas which can be used in commercial practice. Beyond this limit the bed can become unstable or even lift out of the reactor in the gas stream, leading to blockage of the recycle line and damage to the recycle gas compressor or blower. There is also a limit on the extent to which the recycle gas can be cooled in practice. This is primarily determined by economic considerations, and in practise is normally determined by the temperature of the industrial cooling water available on site. Refrigeration can be employed if desired, but this adds to the production costs.

The prior art suggests a number of methods for increasing the heat removal capacity of the recycle stream, for example, by introducing a volatile liquid.

EP 89691 relates to a process for increasing the space time yield in continuous gas fluidised bed processes for the polymerisation of fluid monomers, the process comprising cooling part or all of the unreacted fluids to form a two phase mixture of gas and entrained liquid below the dew point and reintroducing said two phase mixture into the reactor. The specification of EP 89691 states that a primary limitation on the extent to which the recycle gas stream can be cooled below the dew point is in the requirement that the gas-to-liquid ratio be maintained at a level sufficient to keep the liquid phase of the two phase fluid mixture in an entrained or suspended condition until the liquid is vaporised, and further states that the quantity of liquid in the gas phase should not exceed about 20 weight percent, and preferably should not exceed about 10 weight percent, provided always that the velocity of the two phase recycle stream is high enough to keep the liquid phase in suspension in the gas and to support the fluidised bed within the reactor. EP 89691 further discloses that it is possible to form a two-phase fluid stream within the reactor at the point of injection by separately injecting gas and liquid under conditions which will produce a two phase stream, but that there is little advantage seen in operating in this fashion due to the added and unnecessary burden and cost of separating the gas and liquid phases after cooling.

EP 173261 relates to a particular means for introducing a recycle stream into fluidised bed reactors and, in particular, to a means for introducing a recycle stream comprising a two phase mixture of gas and entrained liquid as described in EP 89691 (supra).

WO 94/25495 describes a fluidised bed polymerisation process comprising passing a gaseous stream

comprising monomer through a fluidised bed reactor in the presence of a catalyst under reactive conditions to produce polymeric product and a stream comprising unreacted monomer gases, compressing and cooling said stream, mixing said stream with feed components and returning a gas and liquid phase to said reactor, a method of determining stable operating conditions which comprises: (a) observing fluidised bulk density changes in the reactor associated with changes in the composition of the fluidising medium; and (b) increasing the cooling capacity of the recycle stream by changing the composition without exceeding the level at which a reduction in the fluidised bulk density or a parameter indicative thereof becomes irreversible.

US 5,436,304 relates to a process for polymerising alpha-olefin(s) in a gas phase reactor having a fluidised bed and a fluidising medium wherein the fluidising medium serves to control the cooling capacity of the reactor and wherein the bulk density function (Z) is maintained at a value equal to or greater than the calculated limit of the bulk density function.

WO 94/28032, the contents of which are hereby incorporated by reference, relates to a continuous gas fluidised bed process in which the recycle gas stream is cooled to a temperature sufficient to form a liquid and a gas. By separating the liquid from the gas and then feeding the liquid directly into the fluidised bed at or above the point at which the gaseous stream passing through the fluidised bed has substantially reached the temperature of the gaseous stream being withdrawn from the reactor, the total amount of liquid which may be reintroduced into the fluidised bed polymerisation reactor for the purpose of cooling the bed by evaporation of the liquid can be increased thereby enhancing the level of cooling to achieve higher levels of productivity.

It has now been found that the recycle gas stream may be separated to form a liquid and a gas in a separator which is integral with the polymerisation reactor.

Thus according to the present invention there is provided a continuous gas fluidised bed process for the polymerisation of olefin monomer selected from (a) ethylene, (b) propylene (c) mixtures of ethylene and propylene, and (d) one or more other alpha-olefins mixed with (a), (b) or (c), to produce a polymer in a fluidised bed reactor which process comprises :

(1) continuously recycling a gaseous stream comprising at least some of the olefin monomer through a fluidised bed in said reactor in the presence of a polymerisation catalyst under reactive conditions;
(2) cooling at least part of said gaseous stream withdrawn from said reactor to a temperature at which liquid condenses out and separating at least part of the condensed liquid from the gaseous stream; and
(3) introducing at least part of the separated liquid directly into the fluidised bed,

characterised in that the condensed liquid is separated

from the gaseous stream in a separator which is integral with the fluidised bed reactor.

The advantage of the process of the present invention is that by having the separator integral with the reactor, the plant required for operating the process is greatly simplified.

The present invention also provides a fluidised bed polymerisation reactor for use in a continuous gas fluidised bed process for the polymerisation of olefin monomer selected from (a) ethylene, (b) propylene (c) mixtures of ethylene and propylene, and (d) one or more other alpha-olefins mixed with (a), (b) or (c), to produce a polymer characterized in that said fluidised bed reactor comprises at its bottom part an integral gas/liquid separator.

The gaseous recycle stream withdrawn from the reactor comprises unreacted gaseous monomers, and optionally, inert hydrocarbons, inert gases such as nitrogen, reaction activators or moderators such as hydrogen, as well as entrained catalyst and/or polymer particles.

The recycled gaseous stream fed to the reactor additionally comprises sufficient make-up monomers to replace those monomers polymerised in the reactor.

The process according to the present invention is suitable for the manufacture of polyolefins in the gas phase by the polymerisation of one or more olefins at least one of which is ethylene or propylene. Preferred alpha-olefins for use in the process of the present invention are those having from 4 to 8 carbon atoms. However, small quantities of alpha olefins having more than 8 carbon atoms, for example 9 to 18 carbon atoms (e.g. a conjugated diene), can be employed if desired. Thus it is possible to produce homopolymers of ethylene or propylene or copolymers oxyethylene and/or propylene with one or more C_4-C_8 alpha-olefins. The preferred alpha-olefins are but-1-ene, pent-1-ene, hex-1-ene, 4-methylpent-1-ene, oct-1-ene and butadiene Examples of higher olefins that can be copolymerised with the primary ethylene and/or propylene monomer, or as partial replacement for the C_4-C_8 monomer are dec-1-ene and ethylidene norbornene.

When the process is used for the copolymerisation of ethylene and/or propylene with alpha-olefins the ethylene and/or propylene is present as the major component of the copolymer, and preferably is present in an amount of at least 70%, more preferably at least 80% of the total monomers/comonomers.

The process according to the present invention may be used to prepare a wide variety of polymer products for example linear low density polyethylene (LLDPE) based on copolymers of ethylene with but-1-ene, 4-methylpent-1-ene or hex-1-ene and high density polyethylene (HDPE) which can be for example, homopolyethylene or copolymers of ethylene with a small portion of higher alpha olefin, for example, but-1-ene, pent-1-ene, hex-1-ene or 4-methylpent-1-ene.

The liquid which condenses out of the recycle gas-

eous stream can be a condensable monomer, e.g. but-1-ene, hex-1-ene or octene used as a comonomer for the production of LLDPE or may be an inert condensable liquid, eg inert hydrocarbon(s), such as C_4-C_8 alkane(s) or cycloalkane(s), particularly butane, pentane or hexane.

It is important that the liquid should vaporise within the bed under the polymerisation conditions being employed so that the desired cooling effect is obtained and to avoid substantial accumulation of liquid within the bed.

The process is particularly suitable for polymerising olefins at a pressure of between 0.5 and 6 MPa and at a temperature of between 30°C and 130°C. For example for LLDPE production the temperature is suitably in the range 75-90°C and for HDPE the temperature is typically 80-105°C depending on the activity of the catalyst used.

The polymerisation reaction may be carried out in the presence of a catalyst system of the Ziegler-Natta type, consisting of a solid catalyst essentially comprising a compound of a transition metal and of a cocatalyst comprising an organic compound of metal (i.e an organometallic compound, for example an alkylaluminium compound). High-activity catalyst systems have already been known for a number of years and are capable of producing large quantities of polymer in a relatively short time, and thus make it possible to avoid a step of removing catalyst residues from the polymer. These high-activity catalyst systems generally comprise a solid catalyst consisting essentially of atoms of transition metal, of magnesium and of halogen. It is also possible to use a high-activity catalyst consisting essentially of a chromium oxide activated by a heat treatment and associated with a granular support based on a refractory oxide. The process is also suitable for use with metallocene catalysts and Ziegler catalysts supported on silica.

The catalyst may suitably be employed in the form of prepolymer powder prepared beforehand during a prepolymerization stage with the aid of a catalyst as described above The prepolymerization may be carried out by any suitable process, for example, polymerisation in a liquid hydrocarbon diluent or in the gas phase using a batch process, a semi-continuous process or a continuous process.

Preferably, substantially the whole of the recycle gaseous stream is cooled and separated and substantially the whole of the separated liquid is introduced into the fluidised bed.

In a preferred embodiment of the present invention, the recycle gaseous stream is cooled to a temperature at which liquid condenses out and the gaseous stream is reintroduced into the reactor below the bed, for example, below the fluidisation grid if such a grid is employed. At least part of the condensed liquid from the gaseous stream is separated in the region of the reactor below the bed (integral separator). The remainder of the gaseous stream is passed through the fluidised bed. The

separated liquid is withdrawn from the integral separator and is introduced directly into the fluidised bed. This introduction is preferably made at or above the point at which the gaseous stream passing through the fluidised bed has substantially reached the temperature of the gaseous stream being withdrawn from the reactor.

The recycle gaseous stream is suitably cooled by means of a heat exchanger or exchangers to a temperature such that liquid is condensed in the gas stream. Suitable heat exchangers are well known in the art.

The gaseous stream leaving the top of the reactor can entrain a quantity of catalyst and polymer particles and these may be removed if desired from the recycle gaseous stream by means of a cyclone. A small proportion of these particles or fines may remain entrained in the recycle gaseous stream and, after cooling and separating the liquid from the gas, the fines can, if desired, be reintroduced into the fluidised bed together with the separated liquid stream. Preferably, the fines are reintroduced into the fluidised bed suspended in the liquid stream from the gas/liquid separator.

The recycle gaseous stream may also comprise inert hydrocarbons used for the injection of catalyst, reaction activators or moderators into the reactor.

Make-up monomers for example ethylene to replace monomers consumed by the polymerisation reaction may be added to the recycle gaseous stream at any suitable location.

Condensable monomers, for example, but-1-ene, hex-1-ene, 4-methylpent-1-ene and octene, which can, for example, be used as comonomers for the production of LLDPE, or inert condensable liquids, for example, pentane, isopentane, butane and hexane, may be introduced as liquids.

Inert condensable liquids, for example, pentane may for example be injected into the recycle gaseous stream between the heat exchanger and the point of introduction of the gaseous stream to the integral separator. For the preparation of LLDPE, the comonomer, for example, but-1-ene can, if desired, be injected into the recycle gaseous stream before passage to the heat exchanger.

Suitably, the integral separator may have a volume of between 20 and 80 m^3. Preferably, the diameter of the integral separator is the same as the diameter of the fluidised bed reactor, for example, a diameter of up to 5 metres.

Suitably, a baffle may be situated near the point of introduction of the gaseous stream to the integral separator. This type of integral separator uses the coalescence of liquid droplets on the baffle to separate the condensed liquid from the gas Alternatively, the inlet for the gaseous stream may be arranged tangentially to the walls of the integral separator so that the integral separator acts as a cyclone.

Preferably, a demister is situated immediately below the fluidised bed, for example, below the fluidisation grid if such a grid is employed. Such demisters are well

known in the art.

Preferably, a liquid reservoir is provided in the bottom of the integral separator for collection of the liquid. The liquid reservoir enables the liquid to be stored thereby providing control over the discharge of the liquid from the integral separator and improved control over the cooling of the bed.

Suitably, the residence time in the integral separator is low, for example, in the range 10 seconds to 5 minutes, preferably 30 seconds to 1 minute.

As already discussed hereabove, some particles or fines may remain entrained in the recycle gaseous stream and, after cooling and separating the liquid from the gas, the fines can, if desired, be reintroduced into the fluidised bed together with the liquid stream from the integral separator. In order to keep these particles or fines in suspension and thus avoid fouling of the integral separator it is preferred that the liquid in the integral separator is stirred or that the liquid is continuously circulated, eg by means of an external loop i.e. liquid is continuously withdrawn from and returned to the integral separator. Preferably, the liquid is continuously circulated by means of a pump. Suitably, sufficient liquid is circulated to allow the pump to be operated in a continuous mode. When the level of liquid in the integral separator rises above a certain critical level, as detected by a liquid level controller, a portion of the circulating liquid may be introduced directly into the fluidised bed. Preferably, the portion of the circulating liquid is introduced directly into the fluidised bed via a valve which opens to allow liquid to enter a supply line to the fluidised bed. Preferably, the valve is operated via the liquid level controller.

Applicants have unexpectedly found that when a continuous recirculation of the liquid is used, it is not necessary to separate at the outlet of the reactor the fines and the particles from the recycle gaseous stream. This means that the process can be operated without a cyclone in the recycle loop which is a preferred embodiment according to the present invention.

The separated liquid is thus preferably introduced into the fluidised bed at or above the point at which the gaseous stream passing through the fluidised bed has substantially reached the temperature of the recycle gaseous stream being withdrawn from the reactor. The introduction of the separated liquid may be at a plurality of points within this region of the fluidised bed and these may be at different heights within this region. The point or points of introduction of the liquid are arranged such that the local concentration of liquid does not adversely affect the fluidisation of the bed or the quality of the product, and to enable the liquid to disperse rapidly from each point and vaporise in the bed to remove the heat of polymerisation from the exothermic reaction In this way the amount of liquid introduced for cooling purposes may much more closely approach the maximum loading that can be tolerated without disturbing the fluidisation characteristics of the bed and hence offers the opportunity to achieve enhanced levels of reactor productivity.

The liquid can, if desired, be introduced into the fluidised bed at different heights within the bed Such a technique can facilitate improved control over comonomer incorporation. Controlled metering of liquid into the fluidised bed provides useful additional control over the temperature profile of the bed and, in the case that the liquid contains comonomer, provides useful control over the comonomer incorporation into the copolymer.

The liquid is preferably introduced into the lower part of the region of the fluidised bed at which the recycle gaseous stream has substantially reached the temperature of the gaseous stream being withdrawn from the reactor. Commercial processes for the gas fluidised bed polymerisation of olefins are generally operated under substantially isothermal, steady state conditions. However, although almost all of the fluidised bed is maintained at the desired substantially isothermal polymerisation temperature, there normally exists a temperature gradient in the region of the bed immediately above the point of introduction of the cooled recycle gaseous stream into the bed. The lower temperature limit of this region wherein the temperature gradient exists is the temperature of the incoming cool recycle gas stream, and the upper limit is the substantially isothermal bed temperature. In commercial reactors of the type which employ a fluidisation grid, this temperature gradient normally exists in a layer of about 15 to 30 cm (6 to 12 inches) above the grid.

In order to gain the maximum benefit of the cooling of the separated liquid it is preferred that the liquid is introduced into the bed above the region where this temperature gradient exists, i.e. in the part of the bed which has substantially reached the temperature of the gaseous stream leaving the reactor.

The point or points of introduction of the liquid into the fluidised bed may for example be approximately 50-200 cm, preferably 50-70 cm above the fluidisation grid.

In practice, the temperature profile within the fluidised bed during polymerisation is determined using, for example, thermocouples located in or on the walls of the reactor. Preferably, the point or points of introduction of the liquid is/are then arranged to ensure that the liquid enters into the region of the bed at which the recycle gaseous stream has substantially reached the temperature of the gaseous stream being withdrawn from the reactor.

It is important to ensure that the temperature within the fluidised bed is maintained at a level which is below the sintering temperature of the polyolefin constituting the bed.

If a fluidisation grid is employed, the grid facilitates uniform distribution of the gas from the integral separator to fluidise the bed. The use of fluidisation grid is preferred. Fluidisation grids suitable for use in the process of the present invention can be of conventional design, for example, a flat or dished plate perforated by a plurality of holes distributed more or less uniformly across

its surface. The holes may for example be of diameter of about 5 mm.

The gas velocity in the fluidised bed must be greater than or equal to that required for fluidisation of the bed. The minimum gas velocity is generally approximately 6 cm/sec but the process of the present invention is preferably carried out using a gas velocity in the range 30 to 100, most preferably 50 to 70 cm/sec.

The catalyst or prepolymer caii, if desired, be introduced into the fluidised bed directly with the separated liquid stream. This technique can lead to improved dispersion of the catalyst or prepolymer in the bed.

If desired, liquid or liquid-soluble additives, for example, activators, cocatalysts and the like, can be introduced into the bed together with the condensed liquid by the process according to the present invention.

In the case that the process of the present invention is employed to make ethylene homo- or copolymers, make-up ethylene, for example, to replace the ethylene consumed during the polymerisation, may be advantageously introduced into the separated gas stream prior to its reintroduction into the bed for example below the fluidisation grid if such is employed). By adding the make-up ethylene to the separated gas stream rather than into the gaseous recycle stream before separation, the quantity of liquid which may be recovered from the separator may be increased and the productivity improved.

The separated liquid stream may be subjected to additional cooling (e.g. using refrigeration techniques) before being introduced into the fluidised bed. This allows an even greater cooling effect iii the bed than is provided by the liquid evaporative effect (latent heat of evaporation) alone, thereby providing further potential increases in productivity of the process. Cooling of the separated liquid stream may be achieved by use of suitable cooling means e.g. a simple heat exchanger or refrigerator. A further advantage of this particular aspect of the present invention is that, by cooling the liquid before introduction into the fluidised bed, any tendency for catalyst or prepolymer which may be contained in the liquid stream to cause polymerisation before introduction into the bed will be reduced.

The liquid may be introduced into the fluidised-bed by suitably arranged injection means. A single injection means may be used or a plurality of injection means may be arranged within the fluidised bed.

A preferred arrangement is to provide a plurality of injection means substantially equally spaced in the fluidised bed in the region ofthe introduction of the liquid. The number of injection means used is that number which is required to provide sufficient penetrations and dispersion of liquid at each injection means to achieve good dispersion of liquid across the bed. A preferred number of injection means is four.

Each of the injection means may, if desired, be supplied with the separated liquid by means of a common conduit suitably arranged within the reactor. This can be

provided, for example, by means of a conduit passing up through the centre of the reactor.

The injection means are preferably arranged such that they protrude substantially vertically into the fluidised bed, but may be arranged such that they protrude from the walls of the reactor in a substantially horizontal direction.

The rate at which the liquid can be introduced into the bed depends primarily on the degree of cooling desired in the bed, and this in turn depends on the desired rate of production from the bed. The rates of production obtainable from commercial fluidised bed polymerisation processes for the polymerisation of olefins depend, inter alia on the activity of the catalysts employed, and on the kinetics of such catalysts. Thus, for example, when catalysts having very high activity are employed, and high production rates are desired, the rate of liquid addition will be high. Typical rates of liquid introduction may be, for example, in the range 0.25 to 4.9, preferably 0.3 to 4.9 cubic metres of liquid per cubic metre of bed material per hour, or even higher. For conventional Ziegler catalysts of the "superactive" type (i.e. those based on transition metal, magnesium halide and organometallic cocatalyst, the rate of liquid addition may be, for example, in the range 0.5 to 1.5 cubic metres of liquid per cubic metre of bed material per hour.

In the process of the present invention the weight ratio of liquid:total gas which may be introduced into the bed can be for example in the range 1:100 to 2:1, preferably in the range 5:100 to 85:100, most preferably in the range 6:100 to 25:100. By total gas is meant the gas which is returned to the reactor to fluidise the bed together with any gas used to assist in the operation of the injection means, e.g. atomising gas. The atomising gas may suitably be an inert gas, for example, nitrogen but is preferably make-up ethylene.

By injecting the liquid into the fluidised bed in this way any catalyst which is present in the liquid may benefit from the localised cooling effect of the liquid penetration surrounding each injection means which may avoid hot spots and consequent agglomeration.

Any other suitable injection means may be used provided the penetration and dispersion of the liquid into the bed from such means is sufficient to achieve a good dispersion of liquid across the bed.

The preferred injection means is a nozzle or a plurality of nozzles which include gas-induced atomising nozzles in which a gas is used to assist in the injection of the liquid, or liquid-only spray-type nozzles.

Suitable gas-induced atomising nozzles and liquid-only spray nozzles are as described in WO 94/28032.

Other types of nozzle may also be suitable for use in the process of the present invention for example ultrasonic nozzles.

The injection means are suitably nozzles which protrude into the bed through the reactor wall (or through a supporting grid for the bed) and which carry one or more jet outlets to deliver the liquid to the bed.

It is important in the process of the present invention to achieve good dispersion and penetration of the liquid in the bed. Factors which are important in achieving good penetration and dispersion are the momentum and direction of the liquid entering the bed, the number of points of introduction of the liquid per unit crossectional area of the bed, and the spatial arrangement of the points of introduction of the liquid.

It is preferred that the separated condensed liquid is introduced into the reactor as one or more jets of liquid alone, or one or more jets of liquid and gas, from one or more jet outlets, each jet having a horizontal momentum flux in the case of the liquid only jets of at least 100×10^3 Kg s^{-1} m^{-2} x m s^{-1} and in the case of the gas/liquid jets of 200×10^3 Kg s^{-1} m^{-2} x m s^{-1} wherein the horizontal momentum flux is defined as the mass flow rate of liquid (kilogrammes per second) in the horizontal direction per unit crossectional area (square metres) of the jet outlet from which it emerges, multiplied by the horizontal component of the velocity (metres per second) of the jet.

Preferably the momentum flux of each of the liquid or liquid/gas jets is at least 250×10^3 and most preferably at least 300×10^3 Kg s^{-1} m^{-2} x m s^{-1}. Particularly preferred is the use of a horizontal momentum flux in the range 300×10^3 to 500×10^3 Kg s^{-1} m^{-2} x m s^{-1}. In the case that the liquid jet emerges from the jet outlet in a direction other than horizontal, the horizontal component of the velocity of the jet is calculated from Cosine $Q°$ x actual jet velocity, wherein $Q°$ is the angle the jet makes with the horizontal.

The direction of motion of the one or more liquid or liquid/gas jets into the bed is preferably substantially horizontal. In the case that one or more of the jet outlets deliver the liquid or liquid/gas jets in a direction other than horizontal, preferably these are directed at an angle not greater than 45°, most preferably not more than 20° to the horizontal.

The one or more nozzles are suitably each equipped with one or more jet outlets. The number of nozzles, and the number and distribution of the jet outlets are important factors in obtaining good distribution of liquid within the bed. If a plurality of nozzles are employed, they are preferably vertically disposed and spaced horizontally and substantially equidistant from one another. In this case, they are also preferably spaced equidistant from one another and from the vertical wall of the fluidised bed. The number of nozzles per 10 square metres of the horizontal crossectional area of the bed is preferably in the range 1 to 4, most preferably in the range 2 to 3. Where the calculated number is not an integer, it is preferably rounded up to an integer. The number of jet outlets in each nozzle is preferably in the range 1 to 40 most preferably in the range 3 to 16. In the case that the nozzle contains more than one jet outlet, the jet outlets are preferably arranged circumferentially and equidistant from one another around the nozzle.

Each nozzle may be provided with a plurality of outlets of suitable configuration. The outlets may for example comprise circular holes, slots, ellipsoids or other suitable configurations. Each nozzle may comprise a plurality of outlets of varying configuration.

As indicated above, the jets of liquid may consist solely of liquid or may comprise a liquid/gas mixture. Such gas may be merely carried in the liquid, or may be employed to atomise the liquid, or to provide motive force to propel the liquid.

Before commencing the introduction of liquid by use of the process according to the present invention the gas phase fluidised bed polymerisation may be started in a conventional manner for example by charging the bed with particulate polymer particles and then initiating the gas flow through the bed.

When appropriate the liquid may be withdrawn from the integral separator and introduced into the bed, for example using the injection means described above.

Processes according to the present invention will now be illustrated with reference to the accompanying drawings.

The Figures show diagrammatically a process according to the present invention.

Figure 1 illustrates a gas-phase fluidised bed reactor consisting essentially of a reactor body 1 which is generally an upright cylinder having a fluidisation grid 2 located in its base. The reactor body comprises a fluidised bed 3, a velocity reduction zone 4 which is generally of increased cross-section compared to the fluidised bed, and an integral separator 5.

The gaseous reaction mixture leaving the top of the fluidised bed reactor constitutes recycle gaseous stream and is passed via line 6 to an optional cyclone 7 for the separation of the majority of the fines. Removed fines may suitably be returned to the fluidised bed. The recycle gaseous stream leaving the cyclone passes to a first heat exchanger 8 and a compressor 9. A second heat exchanger 10 is present to remove the heat of compression and to cool the gaseous stream to a temperature at which a condensate is formed, after the recycle gaseous stream has passed through the compressor 9.

The heat exchanger or exchangers can be arranged either upstream or downstream of the compressor 9.

After compression and cooling to a temperature such that a condensate is formed, the resultant gas-liquid mixture is passed to the integral separator 5 where the liquid is removed.

The gas from the integral separator 5 is passed via the fluidisation grid 2 to the bed thereby ensuring that the bed is maintained in a fluidised condition.

The separated liquid from the integral separator 5 is passed via line 11 to the reactor 1. A pump 12 is suitably located in line 11.

Catalyst or prepolymer may be fed to the reactor via line 13 into the separated liquid stream.

Product polymer particles may be suitably removed from the reactor via line 14.

Figure 2 illustrates a process according to the

present invention in which liquid from the integral separator 5 is circulated via lines 11 and 15 and by means of a pump 12 located in line 11. When the liquid level in the integral separator 5 rises above a set level, a valve 16 which is operated by the liquid level controller 17, opens to allow liquid to lie fed to the reactor via line 18.

The arrangements shown in the Figures are particularly suitable for use when retrofitting existing gas phase polymerisation reactors using fluidised bed processes.

Claims

1. Continuous gas fluidised bed process for the polymerisation of olefin monomer selected from (a) ethylene, (b) propylene (c) mixtures of ethylene and propylene, and (d) one or more other alpha-olefins mixed with (a), (b) or (c), to produce a polymer in a fluidised bed reactor which process comprises :

    (1) continuously recycling a gaseous stream comprising at least some of the olefin monomer through a fluidised bed in said reactor in the presence of a polymerisation catalyst under reactive conditions;
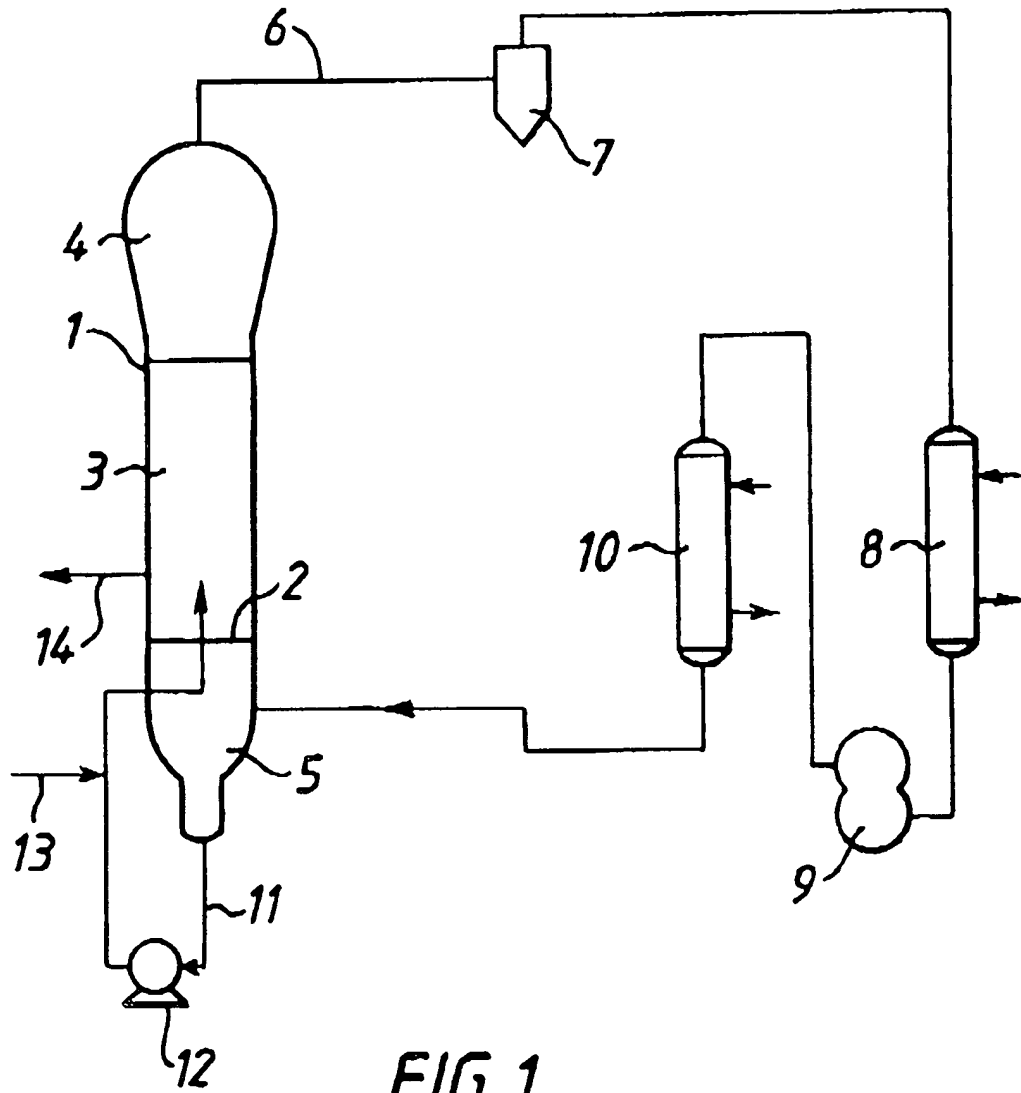   (2) cooling at least part of said gaseous stream withdrawn from said reactor to a temperature at which liquid condenses out and separating at least part of the condensed liquid from the gaseous stream; and
    (3) introducing at least part of the separated liquid directly into the fluidised bed, characterised in that the condensed liquid is separated from the gaseous stream in a separator which is integral with the fluidised bed reactor.

2. Process according to claim 1 wherein the separated liquid is introduced into the fluidised bed at/or above the point at which the gaseous stream passing through the fluidised bed has substantially reached the temperature of the gaseous stream being withdrawn from the reactor.

3. Process according to Claim 1 wherein the separated liquid is introduced into the reactor as one or more jets of liquid alone, or one or more jets of liquid and gas, from one or more jet outlets, each jet having a horizontal momentum flux in the case of the liquid only jets of at least 100×10^{-3} Kg s^{-1} m^{-2} x m s^{-1} and in the case of the gas/liquid jets of 200×10^{3} Kg s^{-1} m^{-2} x m s^{-1} wherein the horizontal momentum flux is defined as the mass flow rate of liquid (kilogrammes per second) in the horizontal direction per unit crossectional area (square metres) of the jet outlet from which it emerges, multiplied by the horizontal component of the velocity (metres per second) of the jet.
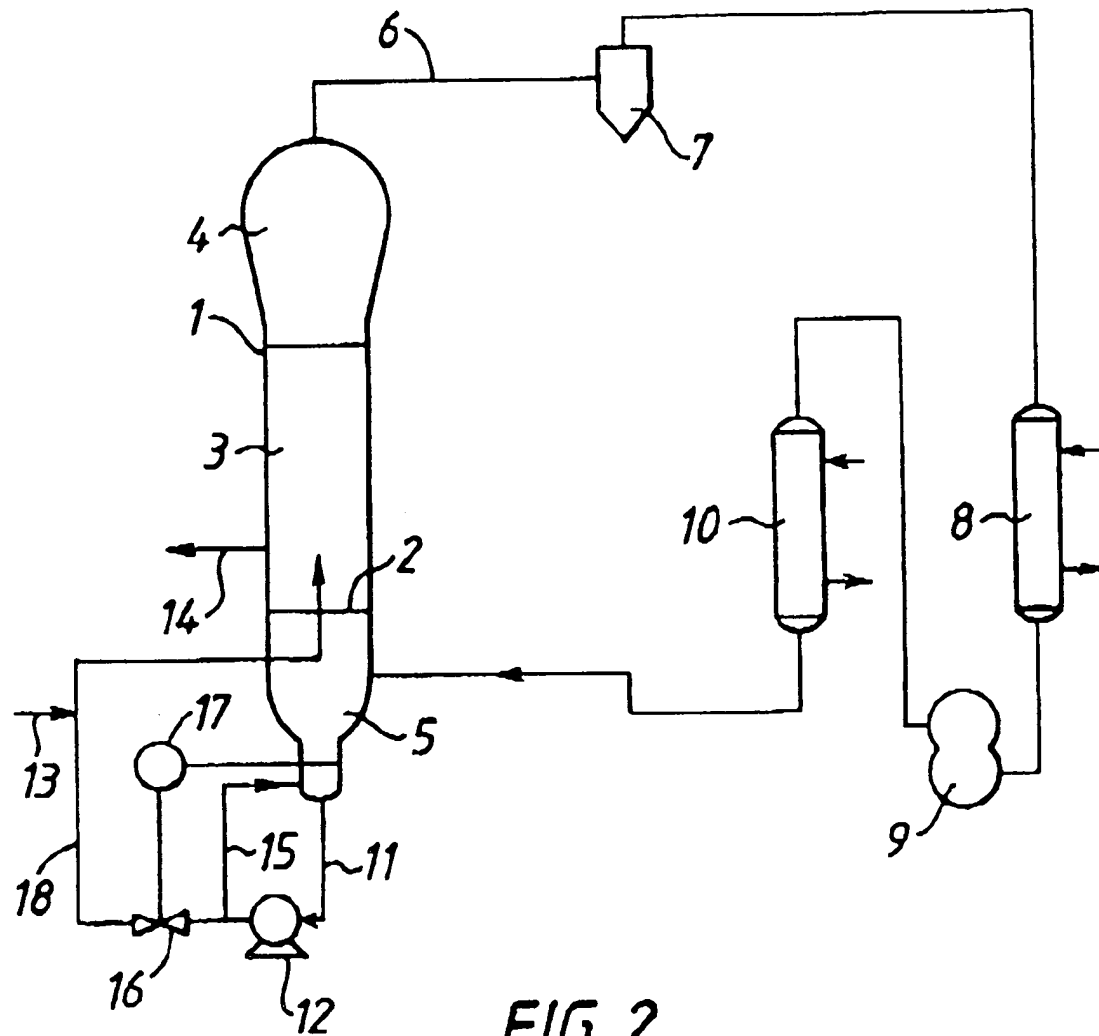
4. Fluidised bed polymerisation reactor for use in a process according to any of the preceding claims characterised in that said fluidised bed reactor comprises at its bottom part an integral gas/liquid separator.

5. Reactor according to claim 4 wherein the integral separator has a circular section having a diameter about the same as the diameter of the reactor.

FIG.1

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FIG. 2

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European Patent Office	EUROPEAN SEARCH REPORT	Application Number EP 97 30 5809

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,A	WO 94 28032 A (BP CHEMICALS INC.) * claims 1-33; figure 3 *	1	C08F10/00 C08F2/34 B01J8/24
A	FR 2 156 037 A (UNIVERSAL OIL PRODUCTS COMPANY) * claims 1-3; figure 1 *	1	
A	GB 754 507 A (ESSO RESEARCH & ENGINEERING COMPANY) * claims 1-12; figure 1 *	1	
A	US 2 870 001 A (G. P. GIUSTI) * claims 1-5; figure 1 *	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6) C08F B01J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24 November 1997	Permentier, W

WHAT IS CLAIMED IS:

1.   Frangible, catalyst support agglomerate particles comprising spray dried inorganic oxide selected from the group consisting of SiO_2, Al_2O_3, MgO, $AlPO_4$, TiO_2, ZrO_2, Cr_2O_3, and mixtures thereof, wherein:

(A)   at least 80% of the volume of the agglomerated particles smaller than the D_{90} of the original agglomerate particle size distribution possesses a microspheroidal morphology;

(B)   the microspheroidal support agglomerate particles possess:

(i) a surface having a rough, scabrous appearance;

(ii) interstitial void spaces having a substantially uniform size and distribution within said agglomerate, with at least some of the interstitial void spaces penetrating the agglomerate particle surface thereby providing at least 10 channels from the agglomerate surface to the agglomerate particle interior; and

(iii) an average IVS of from about 15 to about 40%;

(C)   the support agglomerate particles possess:

(i) an average particle size in the range of about 1 to about 250 microns;

(ii) a surface area of from about 1 to about 1000 m^2 per gram; and

(iii) an AQI of greater than about 10; and

(D)   the constituent particles from which the agglomerate support particles are derived have an average particle size, prior to spray drying, of from about 3 to about 10 microns.

2.   The support agglomerate particles of Claim 1, wherein the AQI thereof is from about 10 to about 70.

5   3.   The support agglomerate particles of Claim 1, wherein the AQI thereof is at least 30.

4.   The support agglomerate particles of Claim 3, wherein the AQI is from about 30 to about 65.

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5.   The support agglomerate particles of Claim 1, wherein the AQI thereof is at least 40.

6.   The support agglomerate particles of Claim 5, 15   wherein the AQI thereof is from about 40 to about 65.

7.   The support agglomerate particles of Claim 1, wherein the AQI thereof is at least 50.

20   8.   The support agglomerate particles of Claim 7, wherein the AQI thereof is from about 50 to about 65.

9.   The support agglomerate particles of any one of
Claims 1-8, wherein:
    (A)   at least 90% of the volume of the agglomerated
particles smaller than the D_{90} of the original
agglomerate particle size distribution possess a
microspheroidal morphology,
    (B)   the support agglomerate particles possess:
        (i)   an average particle size of from about 10
        to about 150 microns, and
        (ii) a surface area of from about 150 to about
        800 m^2/gm.;
    (C)   the constituent particles from which the
support agglomerate particles are derived, prior to
spray drying, have: an average particle size of from
about 4 to about 9 microns, a particle size
Distribution Span of from about 0.5 to about 3.0
microns, and a colloidal particle size content of
from about 2 to about 40 weight %, based on the
constituent particle weight.

10.   The support particles of Claim 9, which have
been impregnated with at least one catalyst component of
a catalyst system capable of polymerizing olefins.

11.   The support particles of Claim 10, wherein the
catalyst component is part of a catalyst system selected
from the group consisting of Ziegler-Natta, metallocene,
and Ni or Pd based catalysts.

12. Frangible, catalyst support agglomerate particles comprising at least 80% by weight, based on the support weight, of spray dried silica gel wherein:

(A) at least 80% of the volume of the agglomerated particles small than the D_{90} of the original agglomerate particle size distribution possess a microspheroidal morphology;

(B) the microspheroidal support agglomerate particles possess:

(i) a surface having a rough, scabrous appearance;

(ii) interstitial void spaces having a substantially uniform size and distribution within said agglomerate, with at least some of the interstitial void spaces penetrating the agglomerate surface thereby providing at least 10 channels from the agglomerate surface to the agglomerate particle interior; and

(iii) an average IVS of from about 15 to about 40%;

(C) the support agglomerate particles possess:

(i) an average particle size in the range of about 1 to about 250 microns;

(ii) a surface area of from about 1 to about 1000 m^2 per gram; and

(iii) an AQI of greater than about 10;

(D) the constituent particles from which the support is derived have an average particle size, prior to spray drying, of from about 3 to about 10 microns; and

(E) the silica gel from which the support agglomerate particles are derived, prior to spray drying, contains from about 2 to about 40 weight %,